

Ozone Production Rates and Efficiencies in 5 Urban Areas:

Why does Houston have the Highest Ozone Concentration in the U.S.?

- Preliminaries

- Monitoring data

- Our data sets

- O_3 chemistry

- Calculations

- Rate of O_3 production

- Multi-city comparison

- Role of VOCs in Houston

- O_3 Production Efficiency

- Multi-city comparison

- Role of VOCs in Houston

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Multi-City Comparison of Ozone Concentration

City	# Flights			P(O ₃)		Max O ₃
	Total	O ₃ >100	O ₃ >120	50 th %	90 th %	
Nashville, 95	17	7	3	6	15	146
NYC, 96	13	4	0	4	15	119
Phoenix. 98	24	1	0	4	8	101
Nashville, 99	4	2	1	-	-	133
Philadelphia, 99	20	6	1	11	22	147
Houston, 2000	18	12	9 ^a	11	39	211

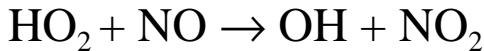
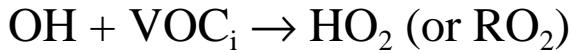
^a 8 flights with O₃ > 150 ppb

"The locales in which we have chosen to conduct these experiments represent very different environments for ozone formation and transport. Conducting experiments in these different venues is a deliberate strategy on our part because we believe that these contrasts constitute important tests of our understanding of the composite meteorological/chemical processes that lead to O₃ formation."

ACP proposal, Daum et al, 2000.

Rates and Efficiencies

Chemistry



In General

$$P(\text{O}_3) \approx \sum k_i Y_i [\text{OH}] [\text{VOC}_i]$$

$$P(\text{NO}_z) \approx k_N [\text{OH}] [\text{NO}_2]$$

$$P(\text{O}_3)/P(\text{NO}_z) \approx \sum k_i Y_i [\text{VOC}_i] / k_N [\text{NO}_2]$$

And, at high NO_x

$$Q = \text{Radical Production Rate} = P(\text{NO}_z)$$

$$P(\text{O}_3) \approx Q \sum k_i Y_i [\text{VOC}_i] / k_N [\text{NO}_2]$$

An aside: at low NO_x

$$P(\text{O}_3) \propto Q^{1/2} [\text{NO}]$$

Calculations

Constrained Steady State (CSS) Box Model

- Inputs from observations

O_3 , NO, VOCs, CO, HCHO, H_2O_2 , ROOH, SO_2 ,
temperature, dew point, pressure, solar intensity

- Model

Input concentrations fixed

Chemical rate expressions for reaction products

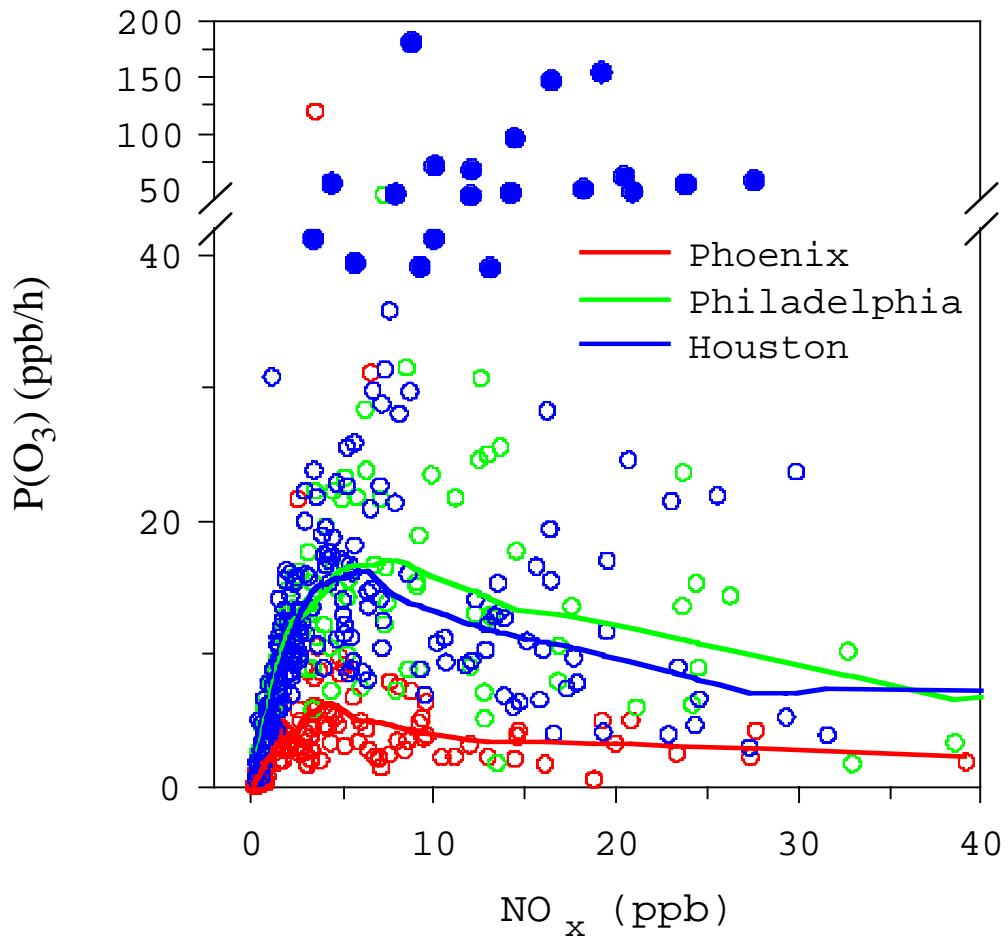
- Outputs

Radical conc: OH, HO_2 , RO_2 's, NO_2

Rates: $P(O_3)$, $P(NO_x)$, etc

Sensitivities: $d\ln P(O_3)/d\ln[NO \text{ or } VOC]$

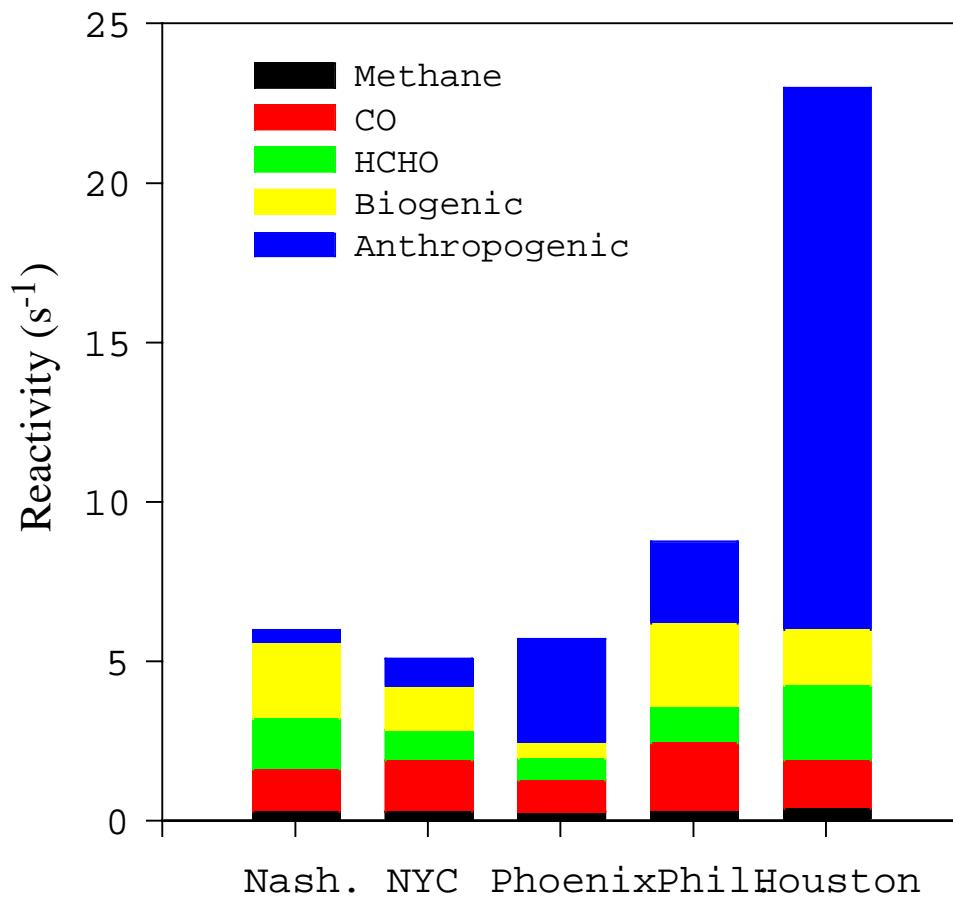
Ozone Production Rates



Reminder: At high NO_x

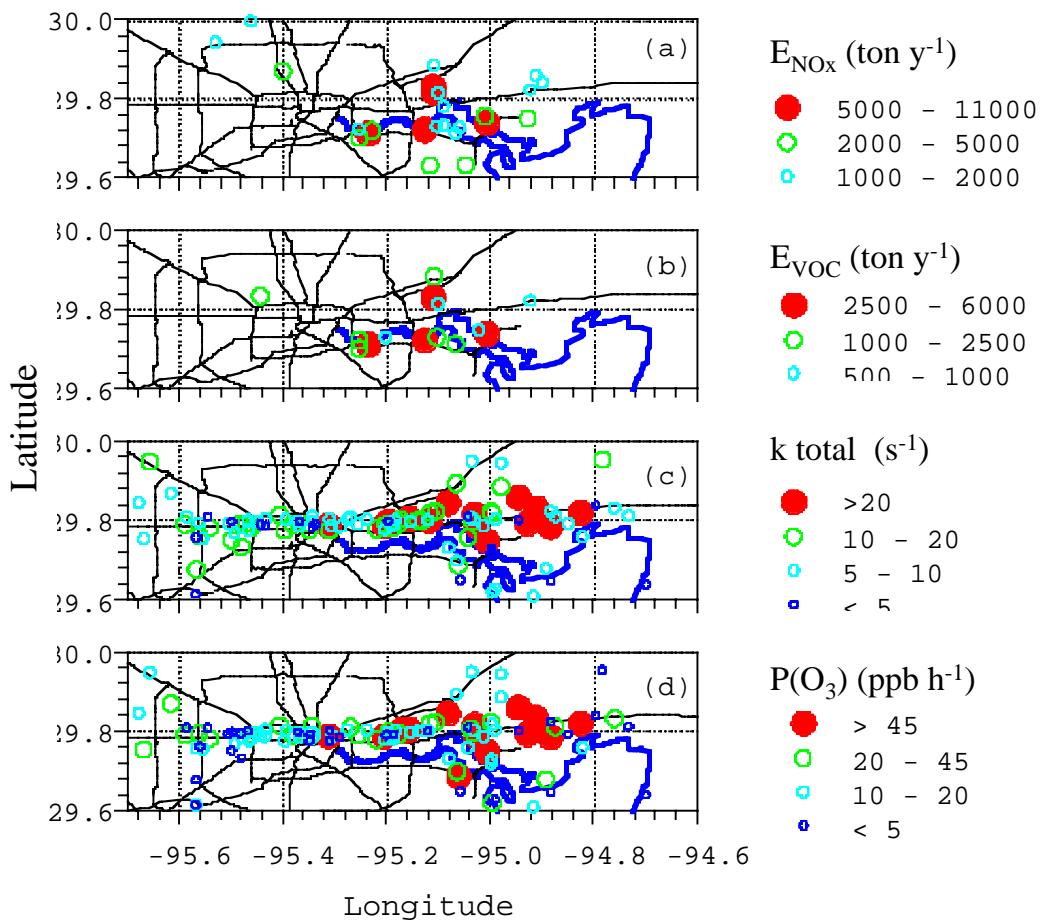
$$P(O_3) \approx Q \sum k_i Y_i [VOC_i] / k_N [NO_2]$$

5 City Comparison of VOC - OH Reactivity



Emssions, VOC Reactivity, P(O₃)

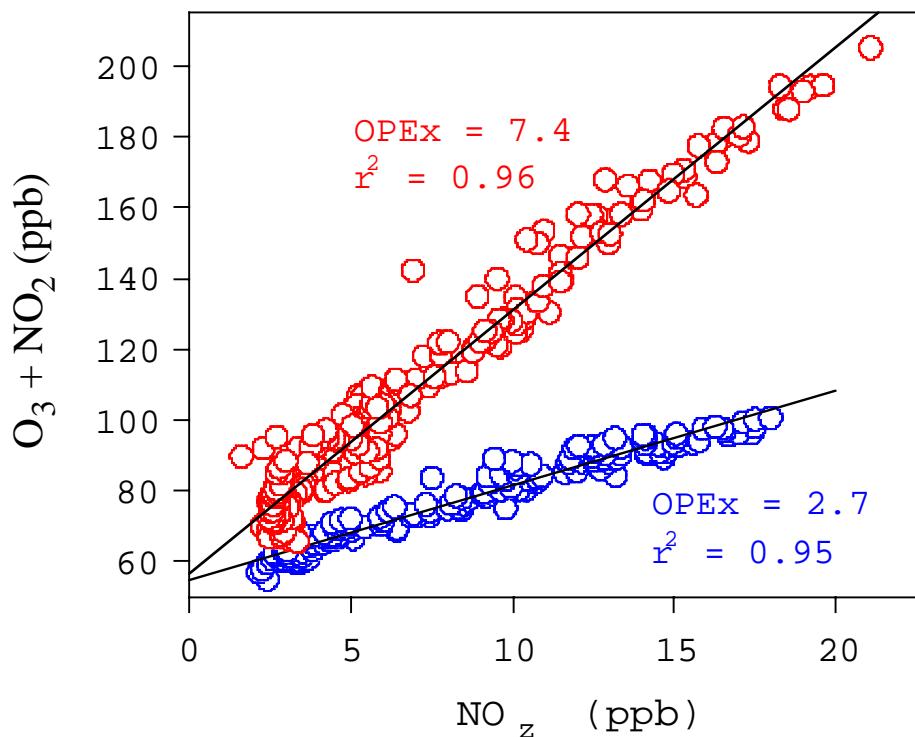
Houston, I10 Corridor



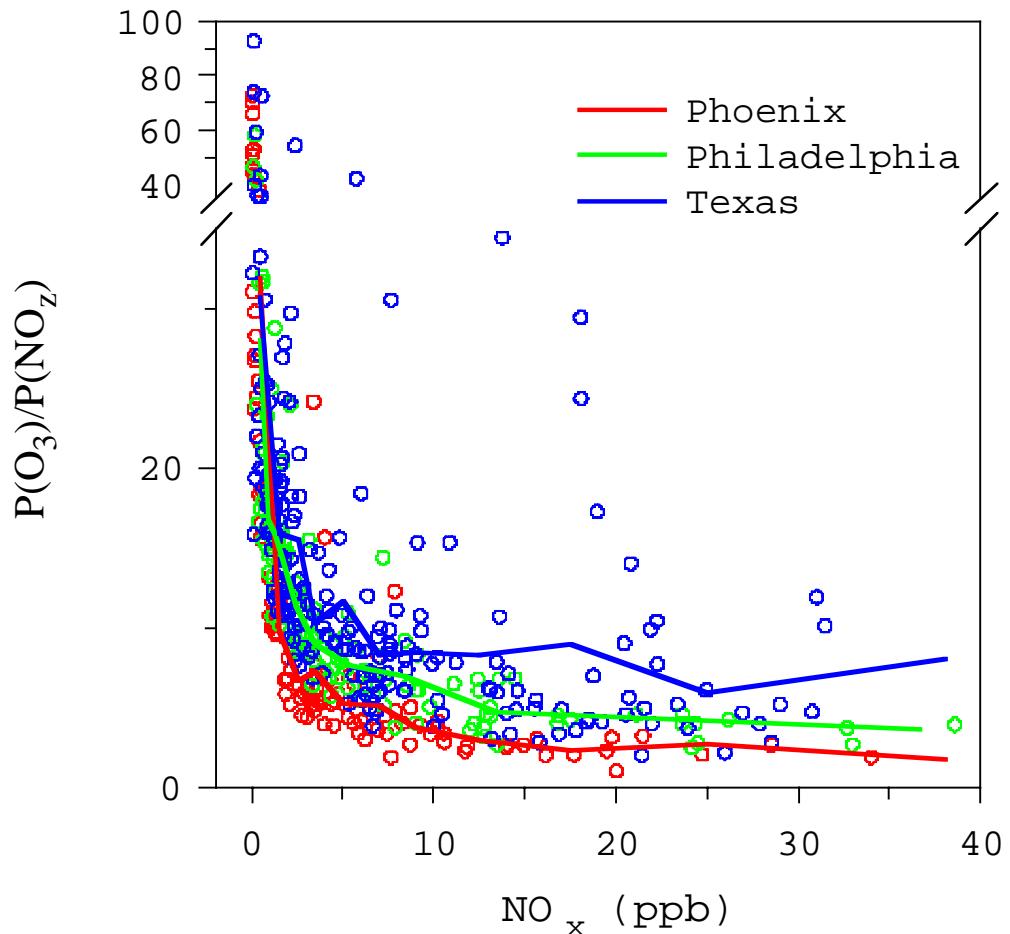
Ozone Production Efficiency

Texas 8/21 PM 2000

Phoenix 6/01 PM 1998



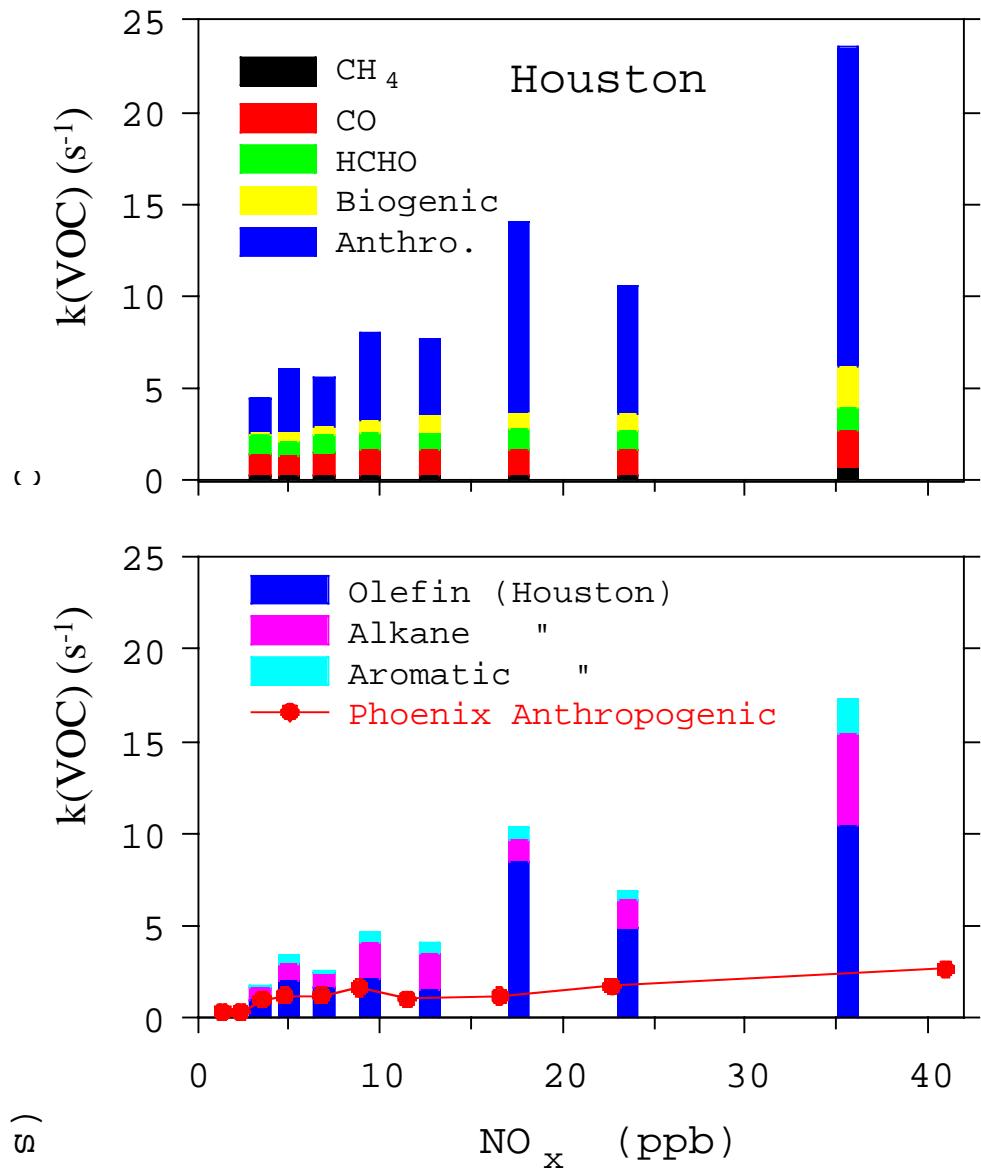
Ozone Production Efficiencies



Reminder:

$$P(O_3)/P(NO_z) \approx \sum k_i Y_i [VOC_i] / k_N [NO_2]$$

VOC - OH Reactivity $\text{M}^{-1} \text{s}^{-1}$



Conclusions

- CSS calculations indicate $P(O_3)$ in 10% of Houston much higher than other cities.
- O_3 production efficiency in Houston higher than other cities.
- High $P(O_3)$ and high OPE caused by high VOC reactivity
- VOC reactivity is from industrial Ship Channel region
- **No reason to believe that Houston is unique!**